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94 Multi-ply films of high impact strength and tear strength, process for their production and their use.

97 The invention relates to a multi-ply film of high impact strength and tear strength, consisting of at least three layers of polyolefin homopolymers and/or copolymers, the two outer layers consisting of thin films of polyolefins of ultrahigh molecular weight and the interposed layer consisting of fibers or fiber structures of polyolefins of ultrahigh molecular weight and the films and the fibers preferably having been stretched to an extreme extent. Due to their small thickness, which, depending on the number of the layers, varies between 0.1 and 100 µm, these multi-ply films are particularly suitable for the manufacture of parachutes, balloons and similar articles, where high impact strength and tear strength in combination with a small film thickness are important.

EP 0 301 624 A2

# MULTI-PLY FILMS OF HIGH IMPACT STRENGTH AND TEAR STRENGTH, PROCESS FOR THEIR PRODUCTION AND THEIR USE

The invention relates to multi-ply films of high impact strength and tear strength, consisting of at least three layers of polyolefin homopolymers and/or copolymers.

Numerous multi-ply films serving the most diverse applications and consisting of layers of polyolefin homopolymers and copolymers or of combinations of such layers with layers of other polymers are known.

5 The known multi-ply films, however, possess good impact strengths and tear strengths only if they are produced in relatively large film thicknesses of several hundred  $\mu\text{m}$ . With such thicknesses, however, they are unsuitable for certain applications such as, for example, for the manufacture of parachutes, balloons and the like, since it is important for these purposes to have available a strong, flexible as well as impact-resistant and tear-resistant material which has a layer thickness of not substantially more than 100  $\mu\text{m}$  and has a low weight per unit area, preferably less than 200  $\text{g/m}^2$ .

10 It was therefore the object of the invention to provide thin multi-ply films, the thickness of which is not substantially more than 100  $\mu\text{m}$  and which have a high impact strength and tear strength.

This object is achieved by the multi-ply films according to the invention of high impact strength and tear strength, consisting of at least three layers of polyolefin homopolymers and/or copolymers, wherein the two 75 outer layers consist of thin films of polyolefins of ultrahigh molecular weight and the interposed layer consists of fibers or fiber structures of polyolefins of ultrahigh molecular weight.

The multi-ply films according to the invention have in general thicknesses of between 0.1 and 100  $\mu\text{m}$ , depending on the number of the layers, and high impact strength and tear strength values and are suitable especially for the manufacture of parachutes, balloons and sails, as building materials, medical implantation 20 materials, for the production of porous filters and the like.

The multi-ply films according to the invention can also be built up from more than the three said layers, that is to say they can also contain one or more further layers of fibers or fiber structures, each of which adjoin layers of films of polyolefins of ultrahigh molecular weight.

The thin films which adjoin the layers of fibers or fiber structures and, in the case of the simplest 25 embodiment of the multiply films according to the invention, form the outer layers, consist preferably, like the fibers or the fibers forming the fiber structures, of polyolefins of ultrahigh molecular weight, the weight-average molecular weight being preferably more than 500,000 and up to 5,000,000  $\text{g/mol}$  or higher in the case of the films and preferably more than 500,000 up to 3,000,000  $\text{g/mol}$  or higher in the case of the fibers.

30 Both the films and the fibers preferably consist of polyethylenes, especially linear polyethylenes, which can contain minor quantities, preferably at most 5  $\text{mol}\%$ , of one or more other alkenes, copolymerizable therewith, such as propylene, butylene, pentene, hexene, 4-methyl-pentene, octene and the like. In the case of fibers, the polyethylenes contain preferably 1 to 10 and especially 2 to 6 methyl or ethyl groups per 1,000 carbon atoms. Other polyolefins can, however, also be used, for example propylene homopolymers and copolymers, and the polyolefins employed can also contain minor quantities of one or more other 35 polymers, especially 1-alkene polymers.

The thin films employed, consisting of polyolefins of ultrahigh molecular weight, preferably have a thickness of between 0.1 and 15  $\mu\text{m}$  and especially between 0.1 and 6  $\mu\text{m}$  and have preferably been stretched, especially biaxially stretched, the product of the stretching in the two main directions (machine 40 direction and the direction transverse thereto) being between 15 and 300.

A particularly preferred process for producing the films employed is described in European patent application filed at the European Patent Office under reference number 5795 on the same date as the present application. This process comprises dissolving the particular polyolefin employed in a solvent, 45 forming the solution at a temperature above the dissolution temperature of the polyolefin to give a tape, cooling the tape, for gelling, to a temperature below the dissolution temperature and then stretching it. In this case, the gel tape is first subjected to a pre-orientation in one direction, while the solvent is being removed, and then stretched at a higher temperature in a direction substantially perpendicular to the direction of the pre-orientation, whereupon final stretching to obtain the finished thin films is carried out. This gives pore-free, i.e. transparent films of high Young moduli, both in the machine direction and in the 50 direction transverse thereto, of more than 6 GPa and elongations at break of between 10 and 100%.

The interlaminar strength of the films employed can have been increased by the process described in European patent application filed at the European Patent Office under reference number 5554 on the same date as the present application in such a way that the films have been subjected to a heat treatment after stretching.

The films employed can also be porous and, in this case, preferably have a density of between 0.1 and 0.9 g/cm<sup>3</sup>. Such porous films can be produced in a known manner, for example by the process known from EP-A-0,183,424, but without applying the compression treatment described therein, for eliminating the pores formed during the evaporation of the solvent from the gel tape. The process described in European patent application filed at the European Patent Office under reference number 5773 on the same date as the present application can also be used for the production of porous films.

Moreover the films employed in the multi-ply films according to the invention can have isotropic or anisotropic properties, that is to say due to the different extents of stretching in the machine direction and in the direction transverse thereto, they can have Young moduli which differ in the said two directions.

The fibers employed for producing the multi-ply films according to the invention preferably have a titer of 0.5 to 10 denier/filament, a tensile strength of more than 10 g/denier and a modulus of more than 500 g/denier, these preferably being uniaxially stretched fibers such as are produced, for example, according to GB-A-2,042,414 and 2,051,667. The uniaxial stretching is here preferably carried out while maintaining a stretching ratio which is preferably between 15 and 150 and especially is 30 or higher.

The fiber layers employed for producing the multi-ply films according to the invention can consist of mono-filaments or multi-filaments, which may have been twisted. The fiber layer can be used in the form of a non-woven, that is to say with an irregular arrangement of the individual fibers, but woven or knitted fabrics can also be used in which the fibers can be perpendicular to one another in the longitudinal and transverse directions or can be arranged at any desired angles. It is also possible to provide more fibers in one direction than the other; for example, there can be more fibers in the machine direction than in the direction transverse thereto, since the impact strengths and tear strengths can in this way be increased in a controlled manner in one direction as compared with the other direction. Moreover, poorer impact strengths and tear strengths, due to an anisotropy, of the films used can be compensated in this way. It is therefore possible, by the selection of films having corresponding anisotropies or by the quantity of the fibers in the machine direction or in the direction perpendicular thereto, to produce tailor-made multi-ply films, which either have properties balanced in the two directions or have different properties.

The impact strengths and tear strengths of the multi-ply films according to the invention are, in the case of the simplest embodiment consisting of two outer films and an interposed fiber layer, at least twice as high as the corresponding properties of a single film, and they are not reduced even in the case of repeated shock and impact effects.

The production of the multi-ply films according to the invention can be carried out in such a way that, in the case of the simplest embodiment, the two films forming the outer layers are pressed together with an interposed nonwoven, woven fabric or knitted fabric of the polyolefin fibres of ultrahigh molecular weight under the action of a temperature which suffices to melt the components instantly on the surface. Preferably, however, a binder is used which, in particular, consists of a thin film, a powder or granules of a polyolefin, such as a polyolefin of low density, which melts at a lower temperature than the polyolefins from which the films or fibers have been produced. This binder then melts under the action of heat and, after cooling, firmly bonds the layers to one another. If desired, other hot-adhesive or cold-adhesive binders known for bonding polyolefin layers can also be used.

The impact strength of the multi-ply films according to the invention is measured by ASTM method D 1709; in this measurement a steel ball of 2 kg weight and 3.8 cm diameter drops from a height of 1 m onto the sample to be tested and the energy (kJ/m) thus absorbed is measured at 23 °C and 50% relative atmospheric humidity.

The tear strength is measured by ASTM method D 1004 (Graves tear strength measurement) at 23 °C and 50% relative atmospheric humidity, the distance between the clamps engaging on the sample being 25.4 mm and the speed at which the clamps move apart being adjusted to 51 mm/minute.

#### Example 1

According to the procedure described in Examples 1 and 6 of European patent application filed at the European Patent Office under reference number 5795 on the same date as the present application, for the continuous production of extremely stretched polyethylene films, a non-porous isotropic film of 4 µm thickness was produced, using a polyethylene of an ultra-high molecular weight (weight-average molecular weight) of about  $1.5 \times 10^6$  g/mol (Hostalen GUR 412®) and using a decalin solution containing 12.5% of the polyethylene.

According to the procedure described in Examples 1 to 3 of GB-A-2,051,667, monofilaments having a titer of 1.8 denier/filament are produced, using the polyethylene of a weight-average molecular weight of

about  $1.5 \times 10^5$  g/mol (Hostalen GUR 412®) and using a decalin solution having a polyethylene concentration of 12.5% by weight, by maintaining the stretching ratio of 30. Two of the polyethylene films produced were pressed together with an interposed fiber fabric and a film of a polyethylene, having a density of  $0.92 \text{ g/cm}^3$  and a melting point of about  $105^\circ \text{C}$ , in a heatable press under a pressure of 15 bar at a temperature of  $110^\circ \text{C}$  for 4 minutes, whereupon the multi-ply film obtained was solidified by cooling. The fiber fabric employed consisted of mutually perpendicular multifilaments arranged at a distance of 4 mm in each case and having a titer of 180 denier, a strength of 33 g/denier, a modulus of 1,350 g/denier and an elongation of 3%, determined at an elongation rate of 50% per minute. The multi-filaments were produced using a monofilament having a titer of 1.8 denier/filament.

For comparison, a multi-ply film without fibers was produced, which had a weight of  $12 \text{ g/cm}^2$ , whereas the weight of the multi-ply film with fibers was  $30 \text{ g/cm}^2$ .

The results of the impact strength and tear strength measurements were as follows:

1. Measurement of the impact strength			
Measurement of the drop energy (kJ/m)			
Sample	Thickness, $\mu\text{m}$	with fibers	without fibers
1	30	400	125
2	26	375	130
3	27	380	170
2. Graves tear strength measurement (maximum stress in MPa)			
Sample	Thickness, $\mu\text{m}$	with fibers	without fibers
1	30	112	23
2	26	70	20
3	27	85	20

## Example 2

Following the procedure described in Example 1, a multi-ply film was produced under a pressure of 5 bar and at a temperature of  $110^\circ \text{C}$  and at a residence time of 7 minutes in the heating press, using porous polyethylene films which had been produced as follows:

Polyethylene of a molecular weight of  $1.5 \times 10^5$  g/mol (Hostalen GUR 412®) was dissolved in decalin by the procedure described in Example 1 to a concentration of 15% by weight, whereupon 1% of a stabilizer, relative to the polyethylene, was added. The solution was formed in the manner described in Example 1 to give a tape, from which the solvent was removed in an oven at  $80^\circ \text{C}$  over a period of 24 hours without allowing shrinkage.  $70 \times 70 \text{ mm}$  samples were cut out of the opaque porous film obtained and biaxially stretched in a stretching ratio of  $10 \times 10$  at a speed of 40 mm/second at  $120^\circ \text{C}$  up to an end thickness of  $3 \mu\text{m}$ .

Fibers were produced by the procedure likewise described in Example 1.

A  $5 \mu\text{m}$  thick film consisting of a linear polyethylene of low density (LLDPE) of  $0.92 \text{ g/cm}^3$  and of melting point  $105^\circ \text{C}$  and provided with holes of 8 mm diameter located at a spacing of 4 mm on all sides was pressed at  $110^\circ \text{C}$  under a pressure of 56 bar for 7 minutes together with a fiber fabric as described in Example 1 and the porous film produced in the manner described above.

The water permeability of the composite material obtained was  $1,200 \text{ g/m}^2/\text{day}$  at  $20^\circ \text{C}$ , measured according to DIN 53122.

## Claims

1. A multi-ply film of high impact strength and tear strength, consisting of at least three layers of polyolefin homopolymers and/or copolymers, wherein the two outer layers consist of thin films of polyolefins of ultrahigh molecular weight and the interposed layer consists of fibers or fiber structures of polyolefins of ultrahigh molecular weight.
2. A multi-ply film as claimed in claim 1, wherein the films forming the outer layer and/or the fibers forming the interlayer consist of homopolymers and/or copolymers of polyolefins.
3. A multi-ply film as claimed in claim 1 or 2, wherein the films forming the outer layers and/or the fibers forming the interlayer are stretched films or fibers respectively.
4. A multi-ply film as claimed in any of claims 1 to 3, wherein the films forming the outer layers have been biaxially stretched.
5. A multi-ply film as claimed in any of claims 1 to 4, wherein the films forming the outer layers and/or the fibers forming the interlayer have been stretched to an extreme extent.
6. A multi-ply film as claimed in any of claims 1 to 5, wherein the films forming the outer layers are porous.
7. A multi-ply film as claimed in any of claims 1 to 6, wherein the layers are mutually joined by hot pressing.
8. A multi-ply film as claimed in claim 7, wherein the layers are mutually bonded with the use, as a binder, of a polyolefin of low density or of another polyolefin melting at a low temperature.
9. A multi-ply film as claimed in any of claims 1 to 8, wherein the films and/or the fibers consist of polyethylene.
10. A process for producing a multi-ply film as claimed in any of claims 1 to 9, which comprises bonding two films of polyolefins of ultrahigh molecular weight with an interposed layer of fibers or fiber structures of polyolefins of ultrahigh molecular weight under the action of heat and pressure.
11. A process as claimed in claim 10, wherein the binder used is a polyolefin of low density or another polyolefin of low melting point.
12. A process as claimed in claim 11, wherein the binder is used in the form of a film.
13. A process as claimed in claim 11, wherein the binder is used in the form of a powder or granules.
14. The use of a multi-ply film as claimed in any of claims 1 to 13 for the manufacture of parachutes, balloons, sails or porous filters or as a building material or medical implantation material.